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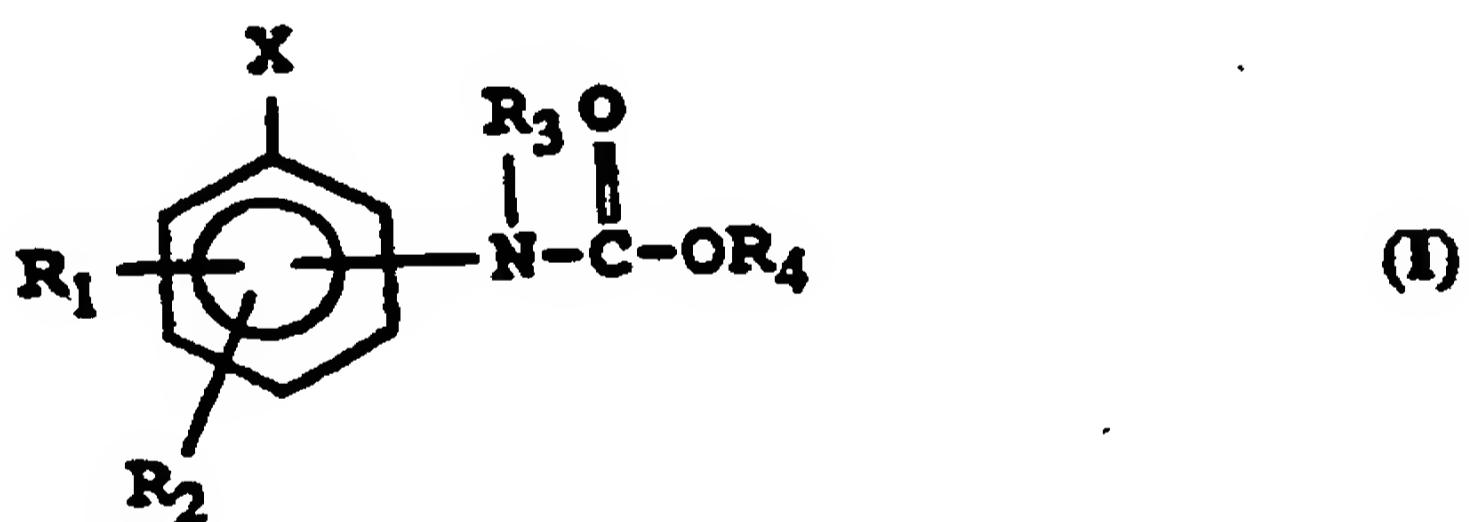
## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(54) Title: **POLYALKYL HYDROXY AND AMINO AROMATIC CARBAMATES AND FUEL COMPOSITIONS CONTAINING THE SAME**

## (57) Abstract

Polyalkyl hydroxy and amino aromatic carbamates having formula (I) or a fuel-soluble salt thereof; wherein X is hydroxy or amino; R<sub>1</sub> and R<sub>2</sub> are independently hydrogen, hydroxy, lower alkyl having 1 to 6 carbon atoms, lower alkoxy having 1 to 6 carbon atoms, nitro, amino, N-alkylamino wherein the alkyl group contains 1 to 6 carbon atoms, or N,N-dialkylamino wherein each alkyl group independently contains 1 to 6 carbon atoms; R<sub>3</sub> is hydrogen or lower alkyl having 1 to 6 carbon atoms; and R<sub>4</sub> is a polyalkyl group having an average molecular weight in the range of about 400 to 5,000. The polyalkyl hydroxy and amino aromatic carbamates of formula (I) are useful as fuel additives for the prevention and control of engine deposits.



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01            POLYALKYL HYDROXY AND AMINO AROMATIC CARBAMATES  
02            AND FUEL COMPOSITIONS CONTAINING THE SAME

03            BACKGROUND OF THE INVENTION

06            Field of the Invention

07            This invention relates to novel hydroxy and amino aromatic  
08            compounds. More particularly, this invention relates to  
09            novel polyalkyl hydroxy and amino aromatic carbamates and  
10            their use in fuel compositions to prevent and control engine  
11            deposits.

13            Description of the Related Art

15            It is well known that automobile engines tend to form  
16            deposits on the surface of engine components, such as  
17            carburetor ports, throttle bodies, fuel injectors, intake  
18            ports and intake valves, due to the oxidation and  
19            polymerization of hydrocarbon fuel. These deposits, even  
20            when present in relatively minor amounts, often cause  
21            noticeable driveability problems, such as stalling and poor  
22            acceleration. Moreover, engine deposits can significantly  
23            increase an automobile's fuel consumption and production of  
24            exhaust pollutants. Therefore, the development of effective  
25            fuel detergents or "deposit control" additives to prevent or  
26            control such deposits is of considerable importance and  
27            numerous such materials are known in the art.

29            For example, aliphatic hydrocarbon-substituted phenols are  
30            known to reduce engine deposits when used in fuel  
31            compositions. U.S. Patent No. 3,849,085, issued  
32            November 19, 1974 to Kreuz et al., discloses a motor fuel  
33            composition comprising a mixture of hydrocarbons in the  
34            composition

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01 gasoline boiling range containing about 0.01 to 0.25 volume  
02 percent of a high molecular weight aliphatic  
03 hydrocarbon-substituted phenol in which the aliphatic  
04 hydrocarbon radical has an average molecular weight in the  
05 range of about 500 to 3,500. This patent teaches that  
06 gasoline compositions containing minor amounts of an  
07 aliphatic hydrocarbon-substituted phenol not only prevent or  
08 inhibit the formation of intake valve and port deposits in a  
09 gasoline engine, but also enhance the performance of the  
10 fuel composition in engines designed to operate at higher  
11 operating temperatures with a minimum of decomposition and  
12 deposit formation in the manifold of the engine.

13  
14 Similarly, U.S. Patent No. 4,134,846, issued January 16,  
15 1979 to Machleider et al., discloses a fuel additive  
16 composition comprising a mixture of (1) the reaction product  
17 of an aliphatic hydrocarbon-substituted phenol,  
18 epichlorohydrin and a primary or secondary mono- or  
19 polyamine, and (2) a polyalkylene phenol. This patent  
20 teaches that such compositions show excellent carburetor,  
21 induction system and combustion chamber detergency and, in  
22 addition, provide effective rust inhibition when used in  
23 hydrocarbon fuels at low concentrations.

24  
25 Amino phenols are also known to function as  
26 detergents/dispersants, antioxidants and anti-corrosion  
27 agents when used in fuel compositions. U.S. Patent  
28 No. 4,320,021, issued March 16, 1982 to R. M. Lange, for  
29 example, discloses amino phenols having at least one  
30 substantially saturated hydrocarbon-based substituent of at  
31 least 30 carbon atoms. The amino phenols of this patent are  
32 taught to impart useful and desirable properties to  
33 oil-based lubricants and normally liquid fuels.

34

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01 Nitro phenols have also been employed as fuel additives.  
02 For example, U.S. Patent No. 4,347,148, issued August 31,  
03 1982 to K. E. Davis, discloses nitro phenols containing at  
04 least one aliphatic substituent having at least about 40  
05 carbon atoms. The nitro phenols of this patent are taught  
06 to be useful as detergents, dispersants, antioxidants and  
07 demulsifiers for lubricating oil and fuel compositions.

08

09 In addition, U.S. Patent No. 4,231,759, issued November 4,  
10 1980 to Udelhofen et al., discloses a fuel additive  
11 composition comprising the Mannich condensation product of  
12 (1) a high molecular weight alkyl-substituted  
13 hydroxyaromatic compound wherein the alkyl group has a  
14 number average molecular weight of about 600 to about 3,000,  
15 (2) an amine and (3) an aldehyde. This patent teaches that  
16 such Mannich condensation products provide carburetor  
17 cleanliness when employed alone, and intake valve  
18 cleanliness when employed in combination with a hydrocarbon  
19 carrier fluid.

20

21 U.S. Patent No. 4,859,210, issued August 22, 1989 to Franz  
et al., discloses fuel compositions containing (1) one or  
more polybutyl or polyisobutyl alcohols wherein the  
polybutyl or polyisobutyl group has a number average  
molecular weight of 324 to 3,000, or (2) a poly(alkoxylate)  
of the polybutyl or polyisobutyl alcohol, or (3) a  
carboxylate ester of the polybutyl or polyisobutyl alcohol.  
This patent further teaches that when the fuel composition  
contains an ester of a polybutyl or polyisobutyl alcohol,  
the ester-forming acid group may be derived from saturated  
or unsaturated, aliphatic or aromatic, acyclic or cyclic  
mono- or polycarboxylic acids.

33

34

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01 U.S. Patent No. 3,285,855, issued November 15, 1966 to  
02 Dexter et al., discloses alkyl esters of dialkyl  
03 hydroxybenzoic and hydroxyphenylalkanoic acids wherein the  
04 ester moiety contains from 6 to 30 carbon atoms. This  
05 patent teaches that such esters are useful for stabilizing  
06 polypropylene and other organic material normally subject to  
07 oxidative deterioration. Similar alkyl esters containing  
08 hindered dialkyl hydroxyphenyl groups are disclosed in U.S.  
09 Patent No. 5,196,565, which issued March 23, 1993 to Ross.  
10  
11 U.S. Patent No. 5,196,142, issued March 23, 1993 to Mollet  
12 et al., discloses alkyl esters of hydroxyphenyl carboxylic  
13 acids wherein the ester moiety may contain up to 23 carbon  
14 atoms. This patent teaches that such compounds are useful  
15 as antioxidants for stabilizing emulsion-polymerized  
16 polymers.  
17  
18 U.S. Patent No. 3,933,470, issued January 20, 1976 to Cross  
19 et al., discloses esters of hydroxycarbanilic acid, wherein  
20 the ester moiety is straight or branched alkyl of 1 to  
21 10 carbon atoms, cycloalkyl, benzyl, chlorobenzyl,  
22 methylbenzyl, phenyl, chlorophenyl, methylphenyl, alkenyl of  
23 2 to 6 carbon atoms, monohaloalkenyl, alkynyl of 2 to  
24 6 carbon atoms, monohaloalkynyl, and monomethoxyalkynyl.  
25 This patent teaches such hydroxycarbanilic acid esters as  
26 intermediates in the preparation of alkynyloxy, alkenyloxy  
27 and cyanoalkoxy carbanilic acid esters, which are useful as  
28 herbicides for controlling broadleaf weeds and grasses.  
29  
30 It has now been discovered that certain polyalkyl hydroxy  
31 and amino aromatic carbamates provide excellent control of  
32 engine deposits, especially intake valve deposits, when  
33 employed as fuel additives in fuel compositions.  
34

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01

SUMMARY OF THE INVENTION

02

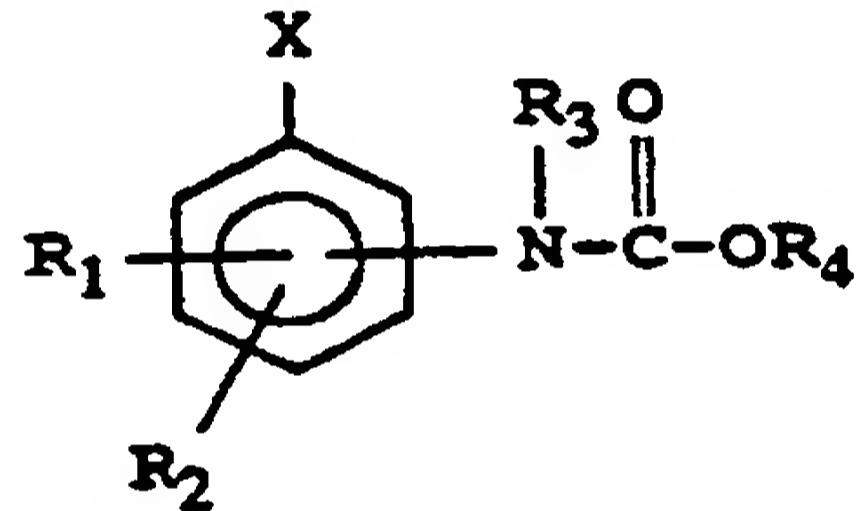
03 The present invention provides novel polyalkyl hydroxy and  
04 amino aromatic carbamates which are useful as fuel additives  
05 for the prevention and control of engine deposits,  
06 particularly intake valve deposits.

07

08 The polyalkyl hydroxy and amino aromatic carbamates of the  
09 present invention are compounds having the formula:

10

11



(I)

12

13

14

15

16

17

18 or a fuel-soluble salt thereof; wherein X is hydroxy or  
19 amino; R<sub>1</sub> and R<sub>2</sub> are independently hydrogen, hydroxy, lower  
20 alkyl having 1 to 6 carbon atoms, lower alkoxy having 1 to 6  
21 carbon atoms, nitro, amino, N-alkylamino wherein the alkyl  
22 group contains 1 to 6 carbon atoms, or N,N-dialkylamino  
23 wherein each alkyl group independently contains 1 to  
24 6 carbon atoms;

25

26 R<sub>3</sub> is hydrogen or lower alkyl having 1 to 6 carbon atoms;  
27 and

28

29 R<sub>4</sub> is a polyalkyl group having an average molecular weight  
30 in the range of about 400 to 5,000.

31

32 The present invention further provides a fuel composition  
33 comprising a major amount of hydrocarbons boiling in the  
34

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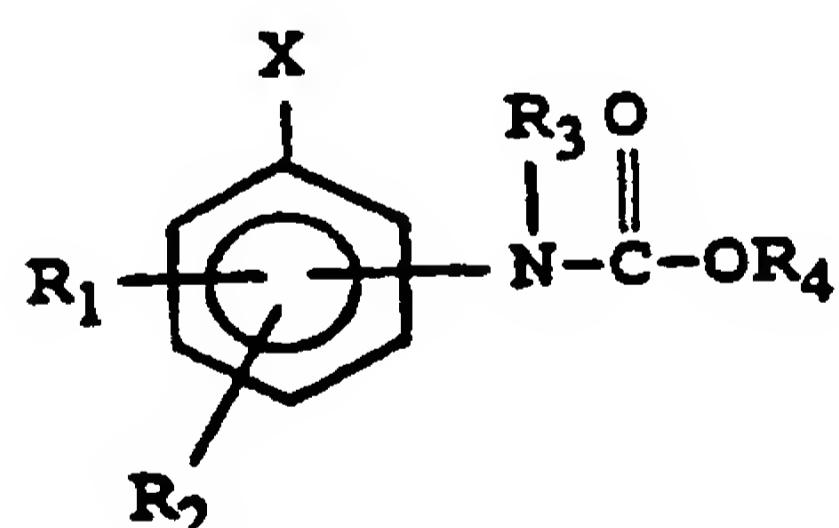
01 gasoline or diesel range and an effective  
02 deposit-controlling amount of a polyalkyl hydroxy or amino  
03 aromatic carbamate of the present invention.

04  
05 The present invention additionally provides a fuel  
06 concentrate comprising an inert stable oleophilic organic  
07 solvent boiling in the range of from about 150°F to 400°F  
08 and from about 10 to 70 weight percent of a polyalkyl  
09 hydroxy or amino aromatic carbamate of the present  
10 invention.

11  
12 Among other factors, the present invention is based on the  
13 surprising discovery that certain polyalkyl hydroxy and  
14 amino aromatic carbamates provide excellent control of  
15 engine deposits, especially on intake valves, when employed  
16 as fuel additives in fuel compositions.

17  
18 DETAILED DESCRIPTION OF THE INVENTION

19  
20 The fuel additives provided by the present invention have  
21 the general formula:



28  
29  
30 or a fuel-soluble salt thereof; wherein X, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, and R<sub>4</sub>  
31 are as defined hereinabove.

32  
33 In formula I above, X can be hydroxy or amino. Preferably,  
34 X is hydroxy.

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01 Preferably, R<sub>1</sub> and R<sub>2</sub> are independently hydrogen, hydroxy,  
02 lower alkyl of 1 to 4 carbon atoms, nitro or amino. More  
03 preferably, R<sub>1</sub> and R<sub>2</sub> are independently hydrogen, hydroxy or  
04 amino. Most preferably, R<sub>1</sub> and R<sub>2</sub> are independently  
05 hydrogen or amino.

06

07 R<sub>3</sub> is preferably hydrogen or lower alkyl of 1 to 4 carbon  
08 atoms. More preferably, R<sub>3</sub> is hydrogen, methyl or ethyl.  
09

10 Preferably, R<sub>4</sub> is a polyalkyl group having an average  
11 molecular weight in the range of about 500 to 3,000, more  
12 preferably about 600 to 2,000,  
13

14 When R<sub>1</sub> or R<sub>2</sub> is an N-alkylamino group, the alkyl group of  
15 the N-alkylamino moiety preferably contains 1 to 4 carbon  
16 atoms. More preferably, the alkyl group is methyl or ethyl.  
17 For example, particularly preferred N-alkylamino groups are  
18 N-methylamino and N-ethylamino groups.  
19

20 Similarly, when R<sub>1</sub> or R<sub>2</sub> is an N,N-dialkylamino group, each  
21 alkyl group of the N,N-dialkylamino moiety preferably  
22 contains 1 to 4 carbon atoms. More preferably, each alkyl  
23 group is either methyl or ethyl. For example, particularly  
24 preferred N,N-dialkylamino groups are N,N-dimethylamino,  
25 N-ethyl-N-methylamino and N,N-diethylamino groups.  
26

27 A preferred group of polyalkyl aromatic carbamates are those  
28 of formula I wherein X is hydroxy; R<sub>1</sub> is hydrogen, hydroxy,  
29 lower alkyl of 1 to 4 carbon atoms, nitro or amino; R<sub>2</sub> is  
30 hydrogen or amino; and R<sub>3</sub> is hydrogen.  
31

32

33 A more preferred group of polyalkyl aromatic carbamates are  
34 those of formula I wherein X is hydroxy; R<sub>1</sub> is hydrogen,

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01 hydroxy or amino; and R<sub>2</sub> and R<sub>3</sub> are hydrogen. Even more  
02 preferably, R<sub>1</sub> is amino and R<sub>2</sub> and R<sub>3</sub> are hydrogen.

03

04 A further preferred group of polyalkyl aromatic carbamates  
05 are those of formula I wherein X is hydroxy; R<sub>1</sub> and R<sub>2</sub> are  
06 amino; and R<sub>3</sub> is hydrogen.

07

08 It is especially preferred that the aromatic hydroxyl or  
09 amino group present in the polyalkyl aromatic carbamates of  
10 this invention be situated in a meta or para position  
11 relative to the polyalkyl carbamate moiety. When the  
12 aromatic moiety contains an additional hydroxy, nitro,  
13 amino, alkylamino or dialkylamino group, it is particularly  
14 preferred that the hydroxyl or amino group be in a meta or  
15 para position relative to the polyalkyl carbamate moiety,  
16 and in an ortho position relative to the additional hydroxy,  
17 nitro, amino, alkylamino or dialkylamino group.

18

19 The polyalkyl hydroxy and amino aromatic carbamates of the  
20 present invention will generally have a sufficient molecular  
21 weight so as to be non-volatile at normal engine intake  
22 valve operating temperatures (about 200-250°C). Typically,  
23 the molecular weight of the polyalkyl hydroxy and amino  
24 aromatic carbamates of this invention will range from about  
25 600 to about 5,000, preferably from 600 to 3,000, more  
26 preferably from 700 to 2,000.

27

28 Fuel-soluble salts of the polyalkyl hydroxy and amino  
29 aromatic carbamates of the present invention are also  
30 contemplated to be useful for preventing or controlling  
31 deposits. For those compounds containing a hydroxy group,  
32 such salts include alkali metal, alkaline earth metal,  
33 ammonium, substituted ammonium and sulfonium salts.

34

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01 Preferred metal salts are the alkali metal salts,  
02 particularly the sodium and potassium salts, and the  
03 substituted ammonium salts, particularly tetraalkyl-  
04 substituted ammonium salts, such as the tetrabutylammonium  
05 salts.

06 Fuel-soluble salts of the polyalkyl aromatic carbamates of  
07 the present invention can also be readily prepared for those  
08 compounds containing an amino, N-alkylamino or  
09 N,N-dialkylamino group. Suitable salts include, for  
10 example, those obtained by protonating the amino moiety with  
11 a strong organic acid, such as an alkyl- or arylsulfonic  
12 acid. Preferred salts are derived from toluenesulfonic acid  
13 and methanesulfonic acid.

15

16 Definitions

17 As used herein, the following terms have the following  
18 meanings unless expressly stated to the contrary.

20

21 The term "amino" refers to the group: -NH<sub>2</sub>.

22

23 The term "N-alkylamino" refers to the group: -NHR<sub>a</sub> wherein  
24 R<sub>a</sub> is an alkyl group. The term "N,N-dialkylamino" refers to  
25 the group: -NR<sub>b</sub>R<sub>c</sub>, wherein R<sub>b</sub> and R<sub>c</sub> are alkyl groups.

26

27 The term "alkyl" refers to both straight- and branched-chain  
28 alkyl groups.

29

30 The term "lower alkyl" refers to alkyl groups having 1 to  
31 about 6 carbon atoms and includes primary, secondary and  
32 tertiary alkyl groups. Typical lower alkyl groups include,

33

34

-10-

01 for example, methyl, ethyl, n-propyl, isopropyl, n-butyl,  
02 sec-butyl, t-butyl, n-pentyl, n-hexyl and the like.

03  
04 The term "lower alkoxy" refers to the group  $-OR_d$  wherein  $R_d$   
05 is lower alkyl. Typical lower alkoxy groups include  
06 methoxy, ethoxy, and the like.

07  
08 The term "polyalkyl" refers to alkyl groups which are  
09 generally derived from polyolefins which are polymers or  
10 copolymers of mono-olefins, particularly 1-mono-olefins,  
11 such as ethylene, propylene, butylene, and the like.  
12 Preferably, the mono-olefin employed will have 2 to about  
13 24 carbon atoms, and more preferably, about 3 to 12 carbon  
14 atoms. More preferred mono-olefins include propylene,  
15 butylene, particularly isobutylene, 1-octene and 1-decene.  
16 Polyolefins prepared from such mono-olefins include  
17 polypropylene, polybutene, especially polyisobutene, and the  
18 polyalphaolefins produced from 1-octene and 1-decene.

19  
20 General Synthetic Procedures

21  
22 The polyalkyl hydroxy and amino aromatic carbamates of this  
23 invention may be prepared by the following general methods  
24 and procedures. It should be appreciated that where typical  
25 or preferred process conditions (e.g., reaction  
26 temperatures, times, mole ratios of reactants, solvents,  
27 pressures, etc.) are given, other process conditions may  
28 also be used unless otherwise stated. Optimum reaction  
29 conditions may vary with the particular reactants or  
30 solvents used, but such conditions can be determined by one  
31 skilled in the art by routine optimization procedures.

32  
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01 Moreover, those skilled in the art will recognize that it  
02 may be necessary to block or protect certain functional  
03 groups while conducting the following synthetic procedures.  
04 In such cases, the protecting group will serve to protect  
05 the functional group from undesired reactions or to block  
06 its undesired reaction with other functional groups or with  
07 the reagents used to carry out the desired chemical  
08 transformations. The proper choice of a protecting group  
09 for a particular functional group will be readily apparent  
10 to one skilled in the art. Various protecting groups and  
11 their introduction and removal are described, for example,  
12 in T. W. Greene and P. G. M. Wuts, *Protective Groups in*  
13 *Organic Synthesis*, Second Edition, Wiley, New York, 1991,  
14 and references cited therein.

15  
16 In the present synthetic procedures, a hydroxyl group will  
17 preferably be protected, when necessary, as the benzyl or  
18 tert-butyldimethylsilyl ether. Introduction and removal of  
19 these protecting groups is well described in the art. Amino  
20 groups may also require protection and this may be  
21 accomplished by employing a standard amino protecting group,  
22 such as a benzyloxycarbonyl or a trifluoroacetyl group.  
23 Additionally, as will be discussed in further detail  
24 hereinbelow, the polyalkyl aromatic carbamates of this  
25 invention having an amino group on the aromatic moiety will  
26 generally be prepared from the corresponding nitro  
27 derivative. Accordingly, in many of the following  
28 procedures, a nitro group will serve as a protecting group  
29 for the amino moiety.

30  
31 The polyalkyl hydroxy and amino aromatic carbamates of the  
32 present invention having the formula:

33

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-12-

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wherein X, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are as defined above, may be prepared by reacting a polyalkyl alcohol having the formula:

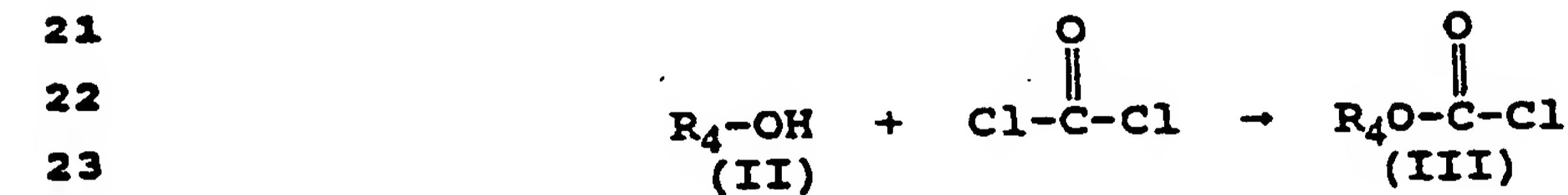
R<sub>4</sub>-OH (II)

wherein R<sub>4</sub> is as defined above, with phosgene, COCl<sub>2</sub>, to provide a chloroformate ester having the formula:



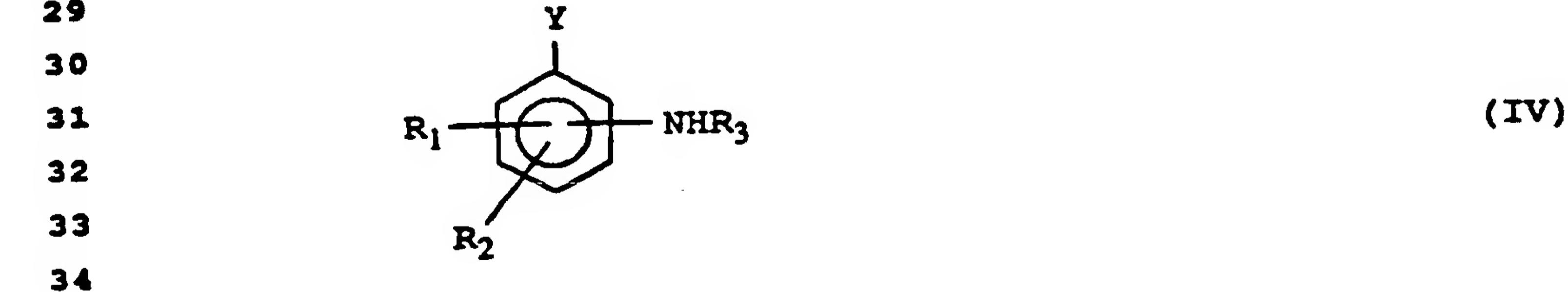
The above reaction may be represented as follows:

20



The resulting chloroformate ester of formula III is then reacted with a primary or secondary hydroxy or nitro aromatic amine having the formula:

28



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01 wherein R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are as defined above, and Y is hydroxy  
 02 or nitro, to provide the polyalkyl hydroxy or nitro aromatic  
 03 carbamates of formula (V). This reaction may be represented  
 04 as follows:

05

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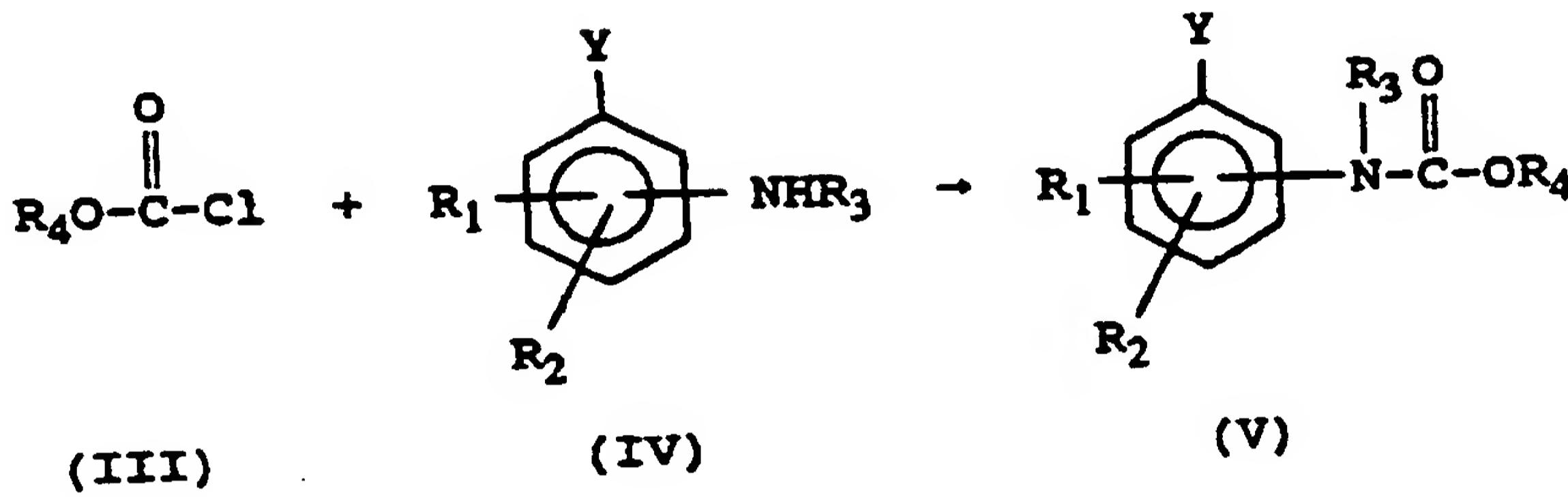
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13 For those compounds of formula V where Y is a nitro group,  
 14 reduction of the nitro group by conventional procedures will  
 15 provide the desired polyalkyl amino aromatic carbamates of  
 16 formula I.

18 The hydroxy or nitro aromatic amines of formula IV are  
 19 either known compounds or can be prepared from known  
 20 compounds by conventional procedures. Suitable hydroxy or  
 21 nitro aromatic amines for use as starting materials in this  
 22 invention include 4-aminophenol, 2-nitro-4-aminophenol,  
 23 2-nitro-5-aminophenol, 2,6-dinitro-4-aminophenol,  
 24 4-(N-methylamino)phenol, 2-nitro-4-(N-methylamino)phenol,  
 25 2-nitro-5-(N-methylamino)phenol,  
 26 2,6-dinitro-4-(N-methylamino)phenol,  
 27 2-hydroxy-4-aminophenol, 2-hydroxy-4-(N-methylamino)phenol,  
 28 2,6-dihydroxy-4-aminophenol,  
 29 2,6-dihydroxy-4-(N-methylamino)phenol,  
 30 2-t-butyl-4-aminophenol, 2-t-butyl-4-(N-methylamino)phenol,  
 31 4-nitroaniline, 3-nitroaniline, and the like.

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- 01 Preferred hydroxy or nitro aromatic amines of formula IV  
02 include 4-aminophenol, 2-nitro-4-aminophenol,  
03 2-nitro-5-aminophenol, 2,6-dinitro-4-aminophenol,  
04 4-nitroaniline and 3-nitroaniline.
- 05
- 06 The polyalkyl alcohols of formula II may also be prepared by  
07 conventional procedures known in the art. Such procedures  
08 are taught, for example, in U.S. Patent Nos. 5,055,607 to  
09 Buckley and 4,859,210 to Franz et al., the disclosures of  
10 which are incorporated herein by reference.
- 11
- 12 In general, the polyalkyl substituent on the polyalkyl  
13 alcohols of formula II and the resulting polyalkyl hydroxy  
14 and amino aromatic carbamates of the present invention will  
15 have an average molecular weight in the range of about 400  
16 to 5,000, preferably about 500 to 3,000, more preferably  
17 about 600 to 2,000.
- 18
- 19 The polyalkyl substituent on the polyalkyl alcohols employed  
20 in the invention may be generally derived from polyolefins  
21 which are polymers or copolymers of mono-olefins,  
22 particularly 1-mono-olefins, such as ethylene, propylene,  
23 butylene, and the like. Preferably, the mono-olefin  
24 employed will have 2 to about 24 carbon atoms, and more  
25 preferably, about 3 to 12 carbon atoms. More preferred  
26 mono-olefins include propylene, butylene, particularly  
27 isobutylene, 1-octene and 1-decene. Polyolefins prepared  
28 from such mono-olefins include polypropylene, polybutene,  
29 especially polyisobutene, and the polyalphaolefins produced  
30 from 1-octene and 1-decene.
- 31
- 32 The preferred polyisobutenes used to prepare the presently  
33 employed polyalkyl alcohols are polyisobutenes which  
34 comprise at least about 20% of the more reactive

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01 methylvinylidene isomer, preferably at least 50% and more  
02 preferably at least 70%. Suitable polyisobutenes include  
03 those prepared using  $\text{BF}_3$  catalysts. The preparation of such  
04 polyisobutenes in which the methylvinylidene isomer  
05 comprises a high percentage of the total composition is  
06 described in U.S. Patent Nos. 4,152,499 and 4,605,808. Such  
07 polyisobutenes, known as "reactive" polyisobutenes, yield  
08 high molecular weight alcohols in which the hydroxyl group  
09 is at or near the end of the hydrocarbon chain.

10  
11 Examples of suitable polyisobutenes having a high  
12 alkylvinylidene content include Ultravis 30, a polyisobutene  
13 having a molecular weight of about 1300 and a  
14 methylvinylidene content of about 74%, and Ultravis 10, a  
15 polyisobutene having a molecular weight of about 950 and a  
16 methylvinylidene content of about 76%, both available from  
17 British Petroleum.

18  
19 The polyalkyl alcohols may be prepared from the  
20 corresponding olefins by conventional procedures. Such  
21 procedures include hydration of the double bond to give an  
22 alcohol. Suitable procedures for preparing such long-chain  
23 alcohols are described in I. T. Harrison and S. Harrison,  
24 *Compendium of Organic Synthetic Methods*, Wiley-Interscience,  
25 New York (1971), pp. 119-122, as well as in U.S. Patent  
26 Nos. 5,055,607 and 4,859,210.

27  
28 As indicated above, the polyalkyl hydroxy and amino aromatic  
29 carbamates of formula I may be prepared by first reacting a  
30 polyalkyl alcohol of formula II with phosgene to form a  
31 chloroformate ester.

32  
33  
34

-16-

01 The reaction of the polyalkyl alcohol of formula II and  
02 phosgene is usually carried out on an essentially equimolar  
03 basis, although excess phosgene can be used to improve the  
04 degree of reaction. Any excess phosgene can be stripped  
05 from the chloroformate ester product prior to reaction with  
06 the hydroxy or nitro aromatic amine. The reaction is  
07 typically carried out at room temperature, although  
08 temperatures in the range of about -10°C to 100°C,  
09 preferably about 0°C to 50°C, may be employed. The reaction  
10 time will usually be in the range of about 0.5 to 48 hours.  
11 The reaction may be conducted in the presence or absence of  
12 an inert solvent, such as benzene, toluene, dichloromethane,  
13 and the like.

14  
15 The resulting chloroformate ester of formula III is then  
16 reacted with a hydroxy or nitro aromatic amine of formula IV  
17 to form the polyalkyl hydroxy or nitro aromatic carbamates  
18 of formula V.

19  
20 The reaction of chloroformate ester with the hydroxy or  
21 nitro aromatic amine will generally be carried out in the  
22 presence of an aprotic solvent, such as methyl cyanide, DMF,  
23 acetone, chloroform, toluene or THF, containing a base  
24 acceptor, such as sodium bicarbonate, sodium carbonate,  
25 triethylamine or pyridine. The reaction will generally be  
26 carried out at room temperature, although higher or lower  
27 temperatures in the range of about -10°C to 100°C may be  
28 employed.

29  
30 The mole ratio of the amine nitrogen to chloroformate ester  
31 will generally be in the range of about 1 to 10 moles of  
32 amine nitrogen per mole of chloroformate ester. The  
33 reaction time may vary from about 0.5 to about 48 hours.  
34 After reaction, the desired product may be isolated by

-17-

01 conventional procedures, such as evaporation of the solvent,  
02 filtration and crystallization.

03

04 Although the polyalkyl hydroxy or amino aromatic carbamates  
05 of the present invention may be conveniently prepared by the  
06 chloroformylation reaction described above, utilizing  
07 phosgene, it is also known in the art that other methods of  
08 producing carbamates are available using other reactants.  
09 For example, the reaction of an isocyanate with an alcohol  
10 also produces a carbamate. Accordingly, it is within the  
11 skill of the art to use a selected isocyanate-substituted  
12 nitro or protected hydroxyaromatic compound to react  
13 directly with a polyalkyl alcohol to provide a carbamate  
14 within the scope of the present invention.

15

16 When necessary, protection of the aromatic hydroxyl groups  
17 on the hydroxyaromatic amines may be accomplished using  
18 well-known procedures. The choice of a suitable protecting  
19 group for a particular hydroxyaromatic amine will be  
20 apparent to those skilled in the art. Various protecting  
21 groups, and their introduction and removal, are described,  
22 for example, in T. W. Greene and P. G. M. Wuts, *Protective*  
23 *Groups in Organic Synthesis*, Second Edition, Wiley,  
24 New York, 1991, and references cited therein.

25

26 Deprotection of the aromatic hydroxyl group(s) can also be  
27 accomplished using conventional procedures. Appropriate  
28 conditions for this deprotection step will depend upon the  
29 protecting group(s) utilized in the synthesis and will be  
30 readily apparent to those skilled in the art. For example,  
31 benzyl protecting groups may be removed by hydrogenolysis  
32 under 1 to about 4 atmospheres of hydrogen in the presence  
33 of a catalyst, such as palladium on carbon. Typically, this  
34 deprotection reaction is conducted in an inert solvent,

-18-

01 preferably a mixture of ethyl acetate and acetic acid, at a  
02 temperature of from about 0°C to about 40°C for about 1 to  
03 about 24 hours.

04  
05 When synthesizing the polyalkyl aromatic carbamates of  
06 formula I having an amino group on the aromatic moiety  
07 (i.e., where X, R<sub>1</sub> and/or R<sub>2</sub> is an amino group), it is  
08 generally desirable to first prepare the corresponding nitro  
09 compound (i.e., where X, R<sub>1</sub> and/or R<sub>2</sub> is a nitro group) and  
10 then to reduce the nitro group to an amino group using  
11 conventional procedures. Aromatic nitro groups may be  
12 reduced to amino groups using a number of procedures that  
13 are well known in the art. For example, aromatic nitro  
14 groups may be reduced under catalytic hydrogenation  
15 conditions; or by using a reducing metal, such as zinc, tin,  
16 iron and the like, in the presence of an acid, such as  
17 dilute hydrochloric acid.

18  
19 Generally, reduction of the nitro group by catalytic  
20 hydrogenation is preferred. Typically, this reaction is  
21 conducted using about 1 to 4 atmospheres of hydrogen and a  
22 platinum or palladium catalyst, such as palladium on carbon.  
23 The reaction is typically carried out at a temperature of  
24 about 0°C to about 100°C for about 1 to 24 hours in an inert  
25 solvent, such as ethanol, ethyl acetate and the like.

26 Hydrogenation of aromatic nitro groups is discussed in  
27 further detail in, for example, P. N. Rylander, *Catalytic*  
28 *Hydrogenation in Organic Synthesis*, pp. 113-137, Academic  
29 Press (1979); and *Organic Synthesis, Collective Vol. I,*  
30 Second Edition, pp. 240-241, John Wiley & Sons, Inc. (1941);  
31 and references cited therein.

32

33

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-19-

Fuel Compositions

- 01
- 02
- 03     The polyalkyl hydroxy and amino aromatic carbamates of the
- 04     present invention are useful as additives in hydrocarbon
- 05     fuels to prevent and control engine deposits, particularly
- 06     intake valve deposits. The proper concentration of additive
- 07     necessary to achieve the desired deposit control varies
- 08     depending upon the type of fuel employed, the type of
- 09     engine, and the presence of other fuel additives.
- 10
- 11     In general, the concentration of the polyalkyl aromatic
- 12     carbamates of this invention in hydrocarbon fuel will range
- 13     from about 50 to about 2500 parts per million (ppm) by
- 14     weight, preferably from 75 to 1,000 ppm. When other deposit
- 15     control additives are present, a lesser amount of the
- 16     present additive may be used.
- 17
- 18     The polyalkyl aromatic carbamates of the present invention
- 19     may be formulated as a concentrate using an inert stable
- 20     oleophilic (i.e., dissolves in gasoline) organic solvent
- 21     boiling in the range of about 150°F to 400°F (about 65°C to
- 22     205°C). Preferably, an aliphatic or an aromatic hydrocarbon
- 23     solvent is used, such as benzene, toluene, xylene or
- 24     higher-boiling aromatics or aromatic thinners. Aliphatic
- 25     alcohols containing about 3 to 8 carbon atoms, such as
- 26     isopropanol, isobutylcarbinol, n-butanol and the like, in
- 27     combination with hydrocarbon solvents are also suitable for
- 28     use with the present additives. In the concentrate, the
- 29     amount of the additive will generally range from about 10 to
- 30     about 70 weight percent, preferably 10 to 50 weight percent,
- 31     more preferably from 20 to 40 weight percent.
- 32
- 33     In gasoline fuels, other fuel additives may be employed with
- 34     the additives of the present invention, including, for

-20-

01 example, oxygenates, such as t-butyl methyl ether, antiknock  
02 agents, such as methylcyclopentadienyl manganese  
03 tricarbonyl, and other dispersants/detergents, such as  
04 hydrocarbyl amines, hydrocarbyl poly(oxyalkylene) amines, or  
05 succinimides. Additionally, antioxidants, metal  
06 deactivators and demulsifiers may be present.

07  
08 In diesel fuels, other well-known additives can be employed,  
09 such as pour point depressants, flow improvers, cetane  
10 improvers, and the like.

11  
12 A fuel-soluble, nonvolatile carrier fluid or oil may also be  
13 used with the polyalkyl aromatic carbamates of this  
14 invention. The carrier fluid is a chemically inert  
15 hydrocarbon-soluble liquid vehicle which substantially  
16 increases the nonvolatile residue (NVR), or solvent-free  
17 liquid fraction of the fuel additive composition while not  
18 overwhelmingly contributing to octane requirement increase.  
19 The carrier fluid may be a natural or synthetic oil, such as  
20 mineral oil, refined petroleum oils, synthetic polyalkanes  
21 and alkenes, including hydrogenated and unhydrogenated  
22 polyalphaolefins, and synthetic polyoxyalkylene-derived  
23 oils, such as those described, for example, in U.S. Patent  
24 No. 4,191,537 to Lewis, and polyesters, such as those  
25 described, for example, in U.S. Patent Nos. 3,756,793 and  
26 5,004,478 to Robinson and Vogel et al., respectively, and in  
27 European Patent Application Nos. 356,726 and 382,159,  
28 published March 7, 1990 and August 16, 1990, respectively.

29  
30 These carrier fluids are believed to act as a carrier for  
31 the fuel additives of the present invention and to assist in  
32 removing and retarding deposits. The carrier fluid may also  
33 exhibit synergistic deposit control properties when used in  
34

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01 combination with a polyalkyl aromatic carbamate compound of  
02 this invention.

03 The carrier fluids are typically employed in amounts ranging  
04 from about 100 to about 5000 ppm by weight of the  
05 hydrocarbon fuel, preferably from 400 to 3000 ppm of the  
06 fuel. Preferably, the ratio of carrier fluid to deposit  
07 control additive will range from about 0.5:1 to about 10:1,  
08 more preferably from 1:1 to 4:1, most preferably about 2:1.  
09

10 When employed in a fuel concentrate, carrier fluids will  
11 generally be present in amounts ranging from about 20 to  
12 about 60 weight percent, preferably from 30 to 50 weight  
13 percent.  
14

15                           EXAMPLES  
16

17 The following examples are presented to illustrate specific  
18 embodiments of the present invention and synthetic  
19 preparations thereof; and should not be interpreted as  
20 limitations upon the scope of the invention.  
21

22                           Example 1  
23

24                           Preparation of Polyisobutylchloroformate  
25

26 Toluene (100 mL) and phosgene (130 mL of a 20 weight percent  
27 solution dissolved in toluene) were cooled to 0°C under  
28 nitrogen. Polyisobutanol (50.0 grams, molecular weight  
29 average 984, prepared via hydroformylation of Amoco H-100  
30 polyisobutene) dissolved in toluene (100 mL) was added  
31 dropwise. The cooling bath was removed and the reaction was  
32 stirred at room temperature for six hours. The solvent was  
33

34

-22-

01 removed in vacuo to yield 39.5 grams of the desired  
02 chloroformate as a light yellow oil.

03

04

Example 2

05

06

Preparation of

07 Polyisobutyl-N-4-hydroxy-3-nitrophenylcarbamate

08

09 A solution of 39.5 grams of the product from Example 1 in  
10 chloroform (500 mL, filtered through activity 1 basic  
11 alumina) containing 4.54 grams of sodium bicarbonate and  
12 8.32 grams of 4-hydroxy-3-nitroaniline was refluxed for  
13 sixteen hours under nitrogen. The mixture was cooled to  
14 room temperature, diluted with dichloromethane (1.2 L) and  
15 washed once with saturated aqueous sodium bicarbonate  
16 solution, twice with water and once with saturated aqueous  
17 sodium chloride. The organic layer was dried over anhydrous  
18 magnesium sulfate, filtered and concentrated in vacuo to  
19 yield 49.5 grams of a yellow brown oil. The oil was  
20 chromatographed on silica gel eluting with hexane followed  
21 by hexane/ethylacetate/ethanol (9:0.8:0.2) to yield  
22 34.1 grams of the desired product as an orange oil. IR  
23 (neat) 1736, 1708 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 10.4 (s, 1H), 8.2  
24 (bs, 1H), 7.7 (d, 1H), 7.15 (d, 1H), 6.7 (bs, 1H), 4.2 (t,  
25 2H), 0.6-1.8 (m, 137H).

26

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-23-

### Example 3

## **Preparation of**

Polyisobutyl-N-4-hydroxy-3-aminophenylcarbamate

A solution of 22.1 grams of the product from Example 2 in  
200 mL of ethylacetate containing 3.0 grams of 10% palladium  
on charcoal was hydrogenolyzed at 35-40 psi for sixteen  
hours on a Parr low-pressure hydrogenator. Catalyst  
filtration and removal of the solvent in vacuo yielded  
14.7 grams of the desired product as a brown oil. <sup>1</sup>H NMR  
(CDCl<sub>3</sub>) δ 6.9 (bs, 1H), 6.65 (d, 1H), 6.5 (d, 1H), 6.35 (bs,  
1H), 4.15 (t, 2H), 4.0 (bs, 3H), 0.6-1.8 (m, 137H).

### Example 4

## **Preparation of**

### Polyisobutyl-N-4-hydroxyphenylcarbamate

A solution of 19.2 grams of the product prepared as in Example 1 in toluene (150 mL) containing 2.73 grams of 4-hydroxyaniline and 3.8 mL of triethylamine was refluxed for sixteen hours under nitrogen. The mixture was cooled to room temperature, diluted with hexane (450 mL) and washed once with water, once with saturated aqueous sodium bicarbonate solution, and once with saturated aqueous sodium chloride. The organic layer was dried over anhydrous magnesium sulfate, filtered and concentrated in vacuo to yield 27.1 grams of a brown oil. The oil was chromatographed on silica gel eluting with hexane followed by hexane/ethylacetate/ethanol (96:2:2) to yield 11.1 grams of the desired product as a yellow oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$

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01 7.4 (d, 2H), 7.15 (d, 2H), 6.6 (bs, 1H), 4.2 (t, 2H),  
02 0.6-1.8 (m, 137H).

03

04 Example 5

05

06 Single-Cylinder Engine Test

07

08 The test compounds were blended in gasoline and their  
09 deposit reducing capacity determined in an ASTM/CFR  
10 single-cylinder engine test.

11

12 A Waukesha CFR single-cylinder engine was used. Each run  
13 was carried out for 15 hours, at the end of which time the  
14 intake valve was removed, washed with hexane and weighed.  
15 The previously determined weight of the clean valve was  
16 subtracted from the weight of the valve at the end of the  
17 run. The differences between the two weights is the weight  
18 of the deposit. A lesser amount of deposit indicates a  
19 superior additive. The operating conditions of the test  
20 were as follows: water jacket temperature 200°F; vacuum of  
21 12 in Hg, air-fuel ratio of 12, ignition spark timing of  
22 40° BTC; engine speed is 1800 rpm; the crankcase oil is a  
23 commercial 30W oil.

24

25 The amount of carbonaceous deposit in milligrams on the  
26 intake valves is reported for each of the test compounds in  
27 Table I and Table II.

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TABLE I

	Sample <sup>1</sup>	Intake Valve Deposit Weight (in milligrams)		Average
		Run 1	Run 2	
05	Base Fuel	253.4	235.5	244.5
06	Example 2	30.1	23.2	26.7
07	Example 3	9.9	7.2	8.6

09 <sup>1</sup>At 150 parts per million actives (ppma).

TABLE II

	Sample <sup>1</sup>	Intake Valve Deposit Weight (in milligrams)		Average
		Run 1	Run 2	
16	Base Fuel	302.6	300.4	301.5
17	Example 4	5.7	4.5	5.1

18 <sup>1</sup>At 200 parts per million actives (ppma).

20 The base fuel employed in the above single-cylinder engine  
21 tests was a regular octane unleaded gasoline containing no  
22 fuel detergent. The test compounds were admixed with the  
23 base fuel to give concentrations of 150 and 200 ppma (parts  
24 per million actives), as indicated in the tables.

26 The data in Table I and Table II illustrates the significant  
27 reduction in intake valve deposits provided by the polyalkyl  
28 aromatic carbamates of the present invention (Examples 2, 3  
29 and 4) compared to the base fuel.

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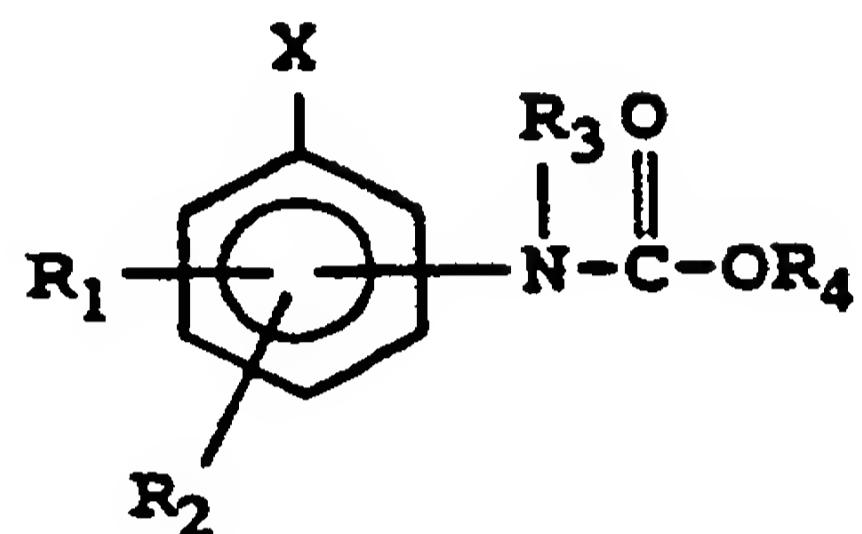
01 WHAT IS CLAIMED IS:

02

03 1. A compound of the formula:

04

05



06

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11

12

or a fuel-soluble salt thereof; wherein

13

14

X is hydroxy or amino;

15

16

R<sub>1</sub> and R<sub>2</sub> are independently hydrogen, hydroxy, lower alkyl having 1 to 6 carbon atoms, lower alkoxy having 1 to 6 carbon atoms, nitro, amino, N-alkylamino wherein the alkyl group contains 1 to 6 carbon atoms, or N,N-dialkylamino wherein each alkyl group independently contains 1 to 6 carbon atoms;

22

23

R<sub>3</sub> is hydrogen or lower alkyl having 1 to 6 carbon atoms; and

25

26

R<sub>4</sub> is a polyalkyl group having an average molecular weight in the range of about 400 to 5,000.

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2. The compound according to Claim 1, wherein R<sub>1</sub> and R<sub>2</sub> are independently hydrogen, hydroxy, lower alkyl of 1 to 4 carbon atoms, nitro or amino; and X is hydroxy.

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- 01 3. The compound according to Claim 2, wherein R<sub>1</sub> and R<sub>2</sub>  
02 are independently hydrogen, hydroxy or amino.
- 03
- 04 4. The compound according to Claim 3, wherein R<sub>1</sub> and R<sub>2</sub>  
05 are independently hydrogen or amino.
- 06
- 07 5. The compound according to Claim 4, wherein R<sub>1</sub> is amino  
08 and R<sub>2</sub> is hydrogen.
- 09
- 10 6. The compound according to Claim 4, wherein R<sub>1</sub> and R<sub>2</sub>  
11 are both amino.
- 12
- 13 7. The compound according to Claim 1, wherein R<sub>3</sub> is  
14 hydrogen or lower alkyl of 1 to 4 carbon atoms.
- 15
- 16 8. The compound according to Claim 1, wherein R<sub>4</sub> is a  
17 polyalkyl group having an average molecular weight in  
18 the range of about 500 to 3,000.
- 19
- 20 9. The compound according to Claim 8, wherein R<sub>4</sub> has an  
21 average molecular weight in the range of about 600 to  
22 2,000.
- 23
- 24 10. The compound according to Claim 1, wherein R<sub>4</sub> is a  
25 polyalkyl group derived from polypropylene, polybutene,  
26 or polyalphaolefin oligomers of 1-octene or 1-decene.
- 27
- 28 11. The compound according to Claim 10, wherein R<sub>4</sub> is  
29 derived from polyisobutene.
- 30
- 31
- 32 12. The compound according to Claim 11, wherein the  
33 polyisobutene contains at least about 20% of a  
34 methylvinylidene isomer.

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- 01 13. A fuel composition comprising a major amount of  
02 hydrocarbons boiling in the gasoline or diesel range  
03 and an effective detergent amount of a compound of the  
04 formula:

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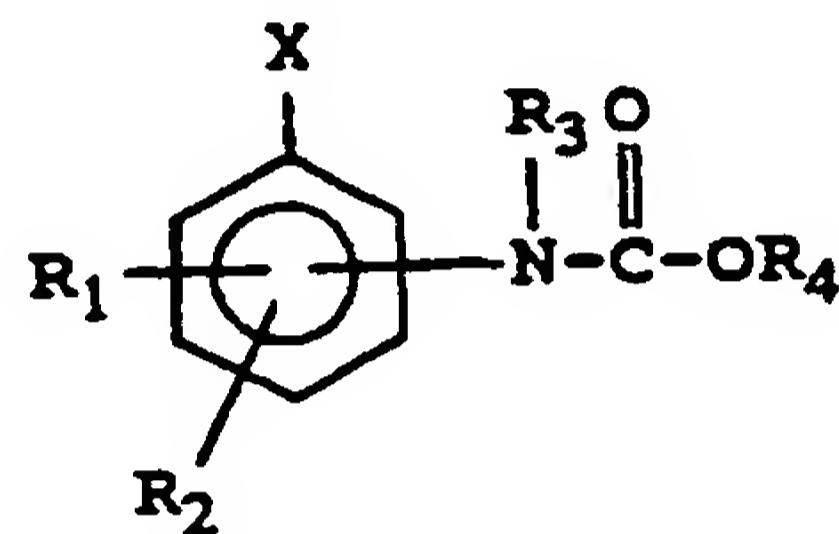
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or a fuel-soluble salt thereof; wherein

X is hydroxy or amino;

R<sub>1</sub> and R<sub>2</sub> are independently hydrogen, hydroxy, lower alkyl having 1 to 6 carbon atoms, lower alkoxy having 1 to 6 carbon atoms, nitro, amino, N-alkylamino wherein the alkyl group contains 1 to 6 carbon atoms, or N,N-dialkylamino wherein each alkyl group independently contains 1 to 6 carbon atoms;

R<sub>3</sub> is hydrogen or lower alkyl having 1 to 6 carbon atoms; and

R<sub>4</sub> is a polyalkyl group having an average molecular weight in the range of about 400 to 5,000.

14. The fuel composition according to Claim 13, wherein R<sub>1</sub> and R<sub>2</sub> are independently hydrogen, hydroxy, lower alkyl of 1 to 4 carbon atoms, nitro or amino; and X is hydroxy.

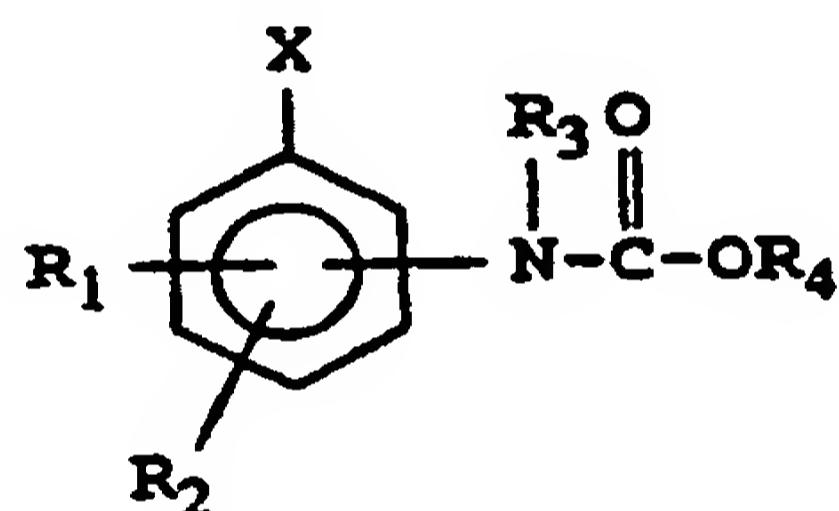
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- 01 15. The fuel composition according to Claim 14, wherein R<sub>1</sub>  
02 and R<sub>2</sub> are independently hydrogen, hydroxy or amino.
- 03
- 04 16. The fuel composition according to Claim 15, wherein R<sub>1</sub>  
05 and R<sub>2</sub> are independently hydrogen or amino.
- 06
- 07 17. The fuel composition according to Claim 16, wherein R<sub>1</sub>  
08 is amino and R<sub>2</sub> is hydrogen.
- 09
- 10 18. The fuel composition according to Claim 16, wherein R<sub>1</sub>  
11 and R<sub>2</sub> are both amino.
- 12
- 13 19. The fuel composition according to Claim 13, wherein R<sub>3</sub>  
14 is hydrogen or lower alkyl of 1 to 4 carbon atoms.
- 15
- 16 20. The fuel composition according to Claim 13, wherein R<sub>4</sub>  
17 is a polyalkyl group having an average molecular weight  
18 in the range of about 500 to 3,000.
- 19
- 20 21. The fuel composition according to Claim 20, wherein R<sub>4</sub>  
21 has an average molecular weight in the range of about  
22 600 to 2,000.
- 23
- 24 22. The fuel composition according to Claim 13, wherein R<sub>4</sub>  
25 is a polyalkyl group derived from polypropylene,  
26 polybutene, or polyalphaolefin oligomers of 1-octene or  
27 1-decene.
- 28
- 29 23. The fuel composition according to Claim 22, wherein R<sub>4</sub>  
30 is derived from polyisobutene.
- 31
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- 01 24. The fuel composition according to Claim 23, wherein the  
02 polyisobutene contains at least about 20% of a  
03 methylvinylidene isomer.
- 04
- 05 25. The fuel composition according to Claim 13, wherein  
06 said composition contains about 50 to about 2500 parts  
07 per million by weight of said compound.
- 08
- 09 26. A fuel concentrate comprising an inert stable  
10 oleophilic organic solvent boiling in the range of from  
11 about 150°F to 400°F and from about 10 to about  
12 70 weight percent of a compound of the formula:
- 13



or a fuel-soluble salt thereof; wherein

X is hydroxy or amino;

R<sub>1</sub> and R<sub>2</sub> are independently hydrogen, hydroxy, lower alkyl having 1 to 6 carbon atoms, lower alkoxy having 1 to 6 carbon atoms, nitro, amino, N-alkylamino wherein the alkyl group contains 1 to 6 carbon atoms, or N,N-dialkylamino wherein each alkyl group independently contains 1 to 6 carbon atoms;

R<sub>3</sub> is hydrogen or lower alkyl having 1 to 6 carbon atoms; and

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- 01        R<sub>4</sub> is a polyalkyl group having an average molecular  
02        weight in the range of about 400 to 5,000.
- 03
- 04        27. The fuel concentrate according to Claim 26, wherein R<sub>1</sub>  
05        and R<sub>2</sub> are independently hydrogen, hydroxy, lower alkyl  
06        of 1 to 4 carbon atoms, nitro or amino; and X is  
07        hydroxy.
- 08
- 09        28. The fuel concentrate according to Claim 27, wherein R<sub>1</sub>  
10        and R<sub>2</sub> are independently hydrogen, hydroxy or amino.
- 11
- 12        29. The fuel concentrate according to Claim 28, wherein R<sub>1</sub>  
13        and R<sub>2</sub> are independently hydrogen or amino.
- 14
- 15        30. The fuel concentrate according to Claim 29, wherein R<sub>1</sub>  
16        is amino and R<sub>2</sub> is hydrogen.
- 17
- 18        31. The fuel concentrate according to Claim 29, wherein R<sub>1</sub>  
19        and R<sub>2</sub> are both amino.
- 20
- 21        32. The fuel concentrate according to Claim 26, wherein R<sub>3</sub>  
22        is hydrogen or lower alkyl of 1 to 4 carbon atoms.
- 23
- 24        33. The fuel concentrate according to Claim 26, wherein R<sub>4</sub>  
25        is a polyalkyl group having an average molecular weight  
26        in the range of about 500 to 3,000.
- 27
- 28        34. The fuel concentrate according to Claim 33, wherein R<sub>4</sub>  
29        has an average molecular weight in the range of about  
30        600 to 2,000.
- 31
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-32-

- 01 35. The fuel concentrate according to Claim 26, wherein R<sub>4</sub>  
02 is a polyalkyl group derived from polypropylene,  
03 polybutene, or polyalphaolefin oligomers of 1-octene or  
04 1-decene.
- 05
- 06 36. The fuel concentrate according to Claim 35, wherein R<sub>4</sub>  
07 is derived from polyisobutene.
- 08
- 09 37. The fuel concentrate according to Claim 36, wherein the  
10 polyisobutene contains at least about 20% of a  
11 methylvinylidene isomer.
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# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US95/04920

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C10L 1/18  
US CL :44/387, 408, 418, 426, 428; 560/24, 132

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 44/387, 408, 418, 426, 428; 560/24, 132

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 4,550,188 (FRULLA ET AL) 29 October 1985, see entire document.	1-12
A	US, A, 4,748,265 (OXBOL ET AL) 31 May 1988, see entire document.	1-12
A	US, A, 5,246,912 (NIELSEN) 21 September 1993, see entire document.	1-12

Further documents are listed in the continuation of Box C.

See patent family annex.

- \* Special categories of cited documents:
  - "A" document defining the general state of the art which is not considered to be of particular relevance
  - "B" earlier document published on or after the international filing date
  - "C" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
  - "D" document referring to an oral disclosure, use, exhibition or other source
  - "E" document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"Z" document member of the same patent family

Date of the actual completion of the international search

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